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(54) Title: UNSATURATED POLYESTER RESINS FLAME RETARDED BY MELAMINE AND PHOSPHORUS COMPOUNDS

(57) Abstract

A flame retarded thermosetting resin composition comprising (A) an unsaturated polyester resin and (B) a vinyl monomer copolymerizable with said resin (A), further comprising an effective flame retardant amount of (C) melamine and (D) a phosphorus compound, and substantially free of halogen and an unesterified polyol. The composition is self-extinguishing, exhibits low smoke evolution upon ignition and has a low density.

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UNSATURATED POLYESTER RESINS FLAME RETARDED BY MELAMINE AND PHOSPHORUS COMPOUNDS

BACKGROUND OF THE INVENTION

The present invention relates to flame retardant unsaturated polyester resin compositions with superior flame retardant characteristics.

Unsaturated thermosetting resin compositions generally comprise a mixture of an unsaturated resin component with an unsaturated compound copolymerisable therewith. Unsaturated polyester resins, crosslinked by vinyl group containing compounds, such as vinylaromatic and/or esterified α,β-unsaturated carboxylic acid compounds comprise an important class of unsaturated thermosetting resins. Generally these resins have a poor resistance to flammability because of their thermal depolymerization when exposed to the heat of a fire, with generation of highly flammable depolymerization products. In the case for instance of unsaturated resins, crosslinked with methyl methacrylate monomers, the monomer itself is evolved. In the case of styrene crosslinked unsaturated resins, styrene dimers and oligomers as well as some styrene are evolved. In this latter case there is not only a flammability problem but also a smoke evolution problem, since aromatic compounds, such as styrene, burn with an inherently sooty flame. Both the flammability and the smoke evolution upon ignition contribute to fire hazard, and limit the areas in which these resins can be safely used without specific measures to reduce their fire hazard.

Known flame retardant unsaturated resins encompass unsaturated polyester resins based on halogenated ingredients, such as tetrachlorophtalic anhydride, tetrabromophtalic anhydride, chlorendic anhydride, dibromoneopentyl glycol, and diallyl

tetrabromophtalate. These all have the disadvantage of being of high specific gravity, an obvious disadvantage for building purposes, and when used in end- products such as small boats or aircraft. A further disadvantage of the use of the above mentioned halogenated ingredients is that they yield corrosive hydrogen halide on combustion. Still a further disadvantage of most of these is the limited photostability. Another family of flame retardant unsaturated resins having the same disadvantages as mentioned above are the unsaturated acrylic resins and vinyl resins incorporating units of tetrabromobisphenol-A in the backbone.

Flame retardant unsaturated polyester resins, free of halogen are also known. These are based on high loadings of mineral fillers, such as alumina trihydrate, gypsum and/or calcium carbonate. These resins also suffer the disadvantage of a high specific gravity. Moreover they often show weathering deficiencies and generally have a high viscosity prior to cure, which is undesirable from a processing point of view.

The use of melamine as a blowing agent has been known in intumescent paint and mastic compounding for many years. In such compositions, a small amount of melamine is employed together with a char-former, such as pentaerythritol or dipentaerythritol, and a charring catalyst, such as ammonium polyphosphate or melamine phosphate. A review of this art can be found in Vandersall, "Intumescent Coating Systems, Their Development and Chemistry", J. of Fire and Flammability, 2, 97-140 (1971). Despite the extensive use of these known formulations containing melamine and phosphorus flame retardants in coatings, the flame retardant usefulness of melamine at higher levels of loading with a phosphorus flame retardant but without a char-forming additive in unsaturated polyester resins

crosslinked by vinylaromatic and/or esterified unsaturated carboxylic acid monomers has not been recognized.

The use of melamine as a flame retardant ingredient in unsaturated resins is itself known in the art. Boockmann, DE-A-2159757 (1973) describes the use of melamine in combination with alumina trihydrate (ATH) in flame retardant unsaturated polyester resins, but requires a special imide-modified unsaturated polyester resin to obtain a satisfactory flame retardancy rating. Pesta, AU-B-307745 (1973) describes the use of melamine itself as a flame retardant in unsaturated polyester resins, but requires a very high loading level of melamine, i.e. 150 parts by weight relative to 100 parts of the resin. These references do not mention phosphorus at all. The use as flame retardant of a melamine phosphate in an unsaturated polyester resin is disclosed in Penczek and Kicko-Walczak, Kunststoffe 77, 415-417 (1977), but a chlorinated unsaturated polyester resin is required for satisfactory flame retardancy. Also the use of melamine itself is not taught in this reference. Godfried, CA-B-914350 (1972) describes the combined use of melamine, a phosphorus source material which yields phosphoric acid on thermal decomposition and a polyhydric alcohol as char-former in flame retardant unsaturated polyester resins. The char-forming polyol is absolutely necessary for satisfactory flame retardancy since the flame retarding mechanism is based on it. Moreover, in order to obtain flame retardancy at least 20 % by weight of the phosphoric acid source and 5 % by weight of the polyhydric alcohol must be present. The flame retarded resin compositions described in CA-B-914350 show a relatively high water sensitivity, which is a considerable disadvantage since mechanical properties are unfavourably affected by water uptake. The advantages of using the combination of melamine and a

phosphorus compound in relatively low amounts and without a char-former in unsaturated polyester resins are not suggested in CA-B-914350, and generally have not been known or suggested in the unsaturated polyester resin art.

The incorporation of low viscosity liquid phosphorus compounds is known as a means for reducing the viscosity of mineral filled unsaturated resins and at the same time boosting flame retardancy of the finished cured resin. The most commonly used phosphorus compounds for this purpose are triethyl phosphate and dimethyl methylphosponate, as discussed by Weil in the "Handbook of Organophosphorus Chemistry", R. Engel, ed., Marcel Dekker, Inc., New York, 1992, Ch. 14, pp. 683-738. A disadvantage of the liquid phosphorus compounds is that they tend to interact with the commonly used accelerators, being soluble cobalt compounds and therefore tend to retard or even inhibit the curing of the unsaturated resins by generally used peroxides.

Other phosphates are sometimes used in such mineral filled formulations to increase flame retardancy or reduce smoke, even if they do not reduce viscosity. An example of such a compound is the bicyclic phosphate of pentaerythritol, described by Termine et al. in US 5,346,938 (1994). It is known also to use ammonium polyphosphate or melamine phosphates as flame retardant in unsaturated polyester resins, but they themselves do not suffice to flame retard the resin. It is therefore usual to employ some other flame retardant modality along with these phosphates. For example, the above cited reference of Penczek and Kicko-Walczak describes the use of a melamine phosphate in a chlorinated unsaturated polyester resin, whereby both the chlorine content and the melamine phosphate contribute to the flame retardant result.

A disadvantage of the solid phosphorus

compounds as flame retardants in unsaturated polyester resins is that they require the use of some halogenated flame retardant or mineral filler, such as ATH to supplement their action. This results in formulations generally having a too high density and viscosity, and showing problems of light stability and corrosivity in the case of the use of halogens.

It is therefore an object of the invention to make available flame retardant unsaturated resin compositions of lower specific gravity than prior flame retardant unsaturated resins.

It is a further object of the invention to make available flame retardant unsaturated resin compositions which do not need halogens in their composition to reach high levels of flame retardancy, despite being crosslinked by compounds such as styrene or methyl methacrylate.

It is a further object of the invention to make available flame retardant unsaturated resin compositions which do not generate excessive amounts of smoke, despite being crosslinked by compounds such as styrene or methyl methacrylate.

It is a further object of the invention to make available flame retardant unsaturated resin compositions which have a reduced water sensitivity compared to hitherto known flame retarded unsaturated resin compositions.

It is a further object of the invention to make available flame retardant unsaturated resin compositions which do not have inhibited cure rates when cobalt salts are used as accelerators for peroxide-based curing.

It is a further object of the invention to make available flame retardant unsaturated resin compositions containing solid flame retardants with a slower settling rate before cure than prior flame retardants, thus obviating prolonged mixing.

It is a further object of the invention to make available flame retardant unsaturated resin compositions which contain synergistically interacting flame retardants such that high degrees of flame retardancy can be achieved with lower loadings of flame retardants than used hitherto.

It is a further object of the invention to make available flame retardant unsaturated resin compositions with low specific gravity, such that they can be used to make more easily carried building panels, which put less weight load on a structure, or add less weight to an aircraft, automobile or boat.

These and other objects are achieved by the compositions described hereunder.

SUMMARY OF THE INVENTION

To achieve the above mentioned objects, the flame retarded thermosetting resin composition according to the invention and comprising (A) an unsaturated polyester resin and (B) a vinyl monomer copolymerizable with said resin (A), is characterized by further comprising an effective flame retardant amount of (C) melamine and (D) a phosphorus compound.

Preferably the resin composition according to the invention is substantially halogen-free, and/or substantially free of a char-forming additive. In particular the preferred resin composition is that which is substantially free of an unesterified polyol.

A further preferred embodiment is that in which the phosphorus compound is a liquid phosphorus ester of lower viscosity than the unsaturated polyester resin itself.

A further preferred embodiment is that in which the phosphorus Compound is a phosphoric acid.

A further preferred embodiment is that in which the resin composition further comprises calcium carbonate and/or calcium sulfate.

DETAILED DESCRIPTION OF THE INVENTION

The unsaturated polyester resin (A) of the invention is any polyester resin mainly synthesized from organic compounds containing carboxyl and alcohol groups. For polyesters diacids and dialcohols are usually used, but up to 40 wt.-% of both types of bifunctional monomers may be replaced by higher-functional monomers or monofunctional monomers or mixtures hereof. Preferably less than 20 wt.-% of both types of bifunctional monomers is replaced by a higher-functional monomer. More in particular, 3-10 wt.-% of one of the two types of bifunctional monomers is replaced by a trifunctional monomer in order to obtain a branched unsaturated polyester. In this manner a higher molar mass is built up within a shorter period of time.

Preferably, at least one ethylenic unsaturated diacid is used. It may be advantageous to terminate the polyester with an unsaturated monocarboxylic acid.

Vinylester polymers, a special class of polyesters, may also be used as component (A) in the composition of the invention. Vinylester polymers are composed of polyols and, possibly, polyacids terminated with acrylate groups, methacrylate groups or other acrylates substituted with C2-C4 alkyl groups at the β position. The polyols may be hydroxyl-terminated polyesters, novolak resins, or polyethers, or, for example, semi-esters of polyols modified with epoxy, isocyanate, polyamine, etc.

The acids that can be used usually contain fewer than 30 carbon atoms, in particular fewer that 20, more in particular fewer than 10 carbon atoms.

As ethylenically unsaturated diacid an α,β-ethylenically unsaturated diacid is preferably used, for example a diacid chosen from the group comprising fumaric acid, maleic acid, chloromaleic acid, itaconic

acid, mesaconic acid, citraconic acid or the corresponding esters or anhydrides.

An ethylenically unsaturated mono- or triacid may be chosen from, for example, the group consisting of linoleic acid or the other unsaturated fatty acids, cinnamic acid, atropic acid, acrylic acid, methacrylic acid, ethacrylic acid, propacrylic acid, crotonic acid, isocrotonic acid or corresponding ester or anhydride derivatives.

Other diacids are preferably saturated aliphatic or aromatic. Aliphatic and aromatic diacids are chosen from, for example, the group : succinic acid, glutaric acid, methylglutaric acid, adipic acid, sebacic acid, pimelic acid, phthalic acid, isophthalic acid, terephthalic acid, dihydrophthalic acid, tetrahydrophthalic acid, tetrachlorophthalic acid, 3,6-endomethylene-1,2,3,6-tetrahydrophthalic acid and hexachloro-endomethylenetetrahydrophthalic acid or the corresponding ester or anhydride derivatives.

Mono- and/or higher-functional aromatic or aliphatic carboxylic acids are chosen from, for example, the group consisting of : benzoic acid, ethylhexanoic acid, mono- or trimeric fatty acids such as stearic acid, acetic acid, propionic acid, pivalic acid, valeric acid, trimellitic acid, 1,2,3,4-butanetetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,4,5,8-naphthalene-tetracarboxylic acid, 1,2,3-propanetricarboxylic acid, 1,2,3-tricarboxylic butane, camphoric acid, naphthoic acid, toluic acid, or the corresponding ester or anhydride derivatives.

The alcohols that may be used usually contain fewer than 30 carbon atoms, in particular fewer than 20 carbon atoms, although particularly ethoxylated or propoxylated bisphenol-A derivatives of polyethylene glycol and polypropylene glycol may contain higher numbers of carbon atoms. Preferably, saturated

aliphatic alcohols or alcohols containing an aromatic group are used. Ethylenically unsaturated alcohols may also be used. Dialcohols are chosen from, for example, the group comprising ethylene glycol, di(ethyleneglycol), tri(ethylene glycol), 1,2-propanediol, dipropylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3 butanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, 1,4-pentanediol, 1,4-hexanediol, 1,6-hexanediol, 2,2-dimethylpropanediol, cyclohexane-diol, 2,2-bis-(hydroxycyclohexyl)-propane, 1,2-trimethylolpropane monoallyl ether, pinacol, bisphenol-A ethoxylated or propoxylated with 1-20 equivalents and novolak prepolymers, if so desired partly etherified and ethoxylated. Instead of a 1,2-diol, the corresponding oxirane compound may be used.

Mono-and higher-functional alcohols are chosen from, for example, the group comprising methanol, ethanol, 1- or 2-propanol, 1- or 2-butanol, one of the isomers of pentanol, hexanol, octanol, 2-ethylhexanol, fatty alcohols, benzyl alcohols, 1,2-di(allyloxy)-3-propanol, glycerol, 1,2,3-propanetriol, pentaerythritol, tris-(hydroxyethyl)isocyanurate and novolak prepolymers, if so desired partly etherified and ethoxylated.

Alkoxilated unsaturated acids are particularly suitable to be used as ethylenically unsaturated alcohols, for example 2-hydroxy-ethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, bis(2-hydroxy-ethyl)fumarate, but also, for example, butenediol.

It is advantageous for the flame retardancy to use an unsaturated polyester modified with dicyclopentadienyl (DCPD) units. Preferably, an unsaturated polyester modified with 2-45 wt.-% DCPD units is used as component (A), more preferably an unsaturated polyester modified with 20-35 wt.-% DCPD units.

The polymers (A) can be manufactured in many ways, for example by melt condensation, solvent condensation with distillative removal of water, whether or not in an azeotropic mixture, by epoxy-acid reactions and other methods known to a person skilled in the art.

The compound (B) copolymerisable with the polyester and containing one or more vinyl groups, usually contains fewer than 50 carbon atoms, preferably fewer than 30 and more in particular fewer than 15, but more than 3 carbon atoms. The compound containing one or more vinyl groups is preferably of the vinylaromatic, vinylether, vinylester, acrylate and/or allyl type. More in particular, a vinylaromatic or acrylate compound is used, because these react quickly in the radical polymerization.

Vinylaromatic compounds are chosen from, for example, the group comprising styrene, α-methylstyrene, o-, m-, p-methylstyrene, p-chlorostyrene, t-butylstyrene, divinylbenzene, bromostyrene, vinylnaphthalene, α-chlorostyrene and divinylnaphthalene.

Acrylate compounds are chosen from, for example, the group comprising methyl, ethyl, propyl, isopropyl, butyl, isobutyl, phenyl, and benzyl acrylate or methacrylate, 2-ethylhexyl (meth)acrylate, dihydrocyclopentadiene acrylate, cyclohexyl (meth)acrylate, butanediol (meth)acrylate, butanediol di(meth)acrylate, (meth)acrylamide, the reaction products of (meth)acrylic acid and phenyl- or cresylglycidyl ethers, propyleneglycol di(meth)acrylate, di- en triethyleneglycol di(meth)acrylate, di- en tripropyleneglycol di(meth)acrylate, hexanedioldi(meth)acrylate, trimethylolpropanetri(meth)acrylate. Derivatives of acrylates substituted with C2-C4 at position β may also be used.

Vinylether, vinylester and allyl compounds are chosen from, for example, the group comprising allylphthalate, diallylphthalate, diallylisophthalate, triallylcyanurate, diallylterephthalate, ethylhexanoic vinylester, vinylacetate, vinylpropionate, vinylpivalate, vinylether, vinylversatate, vinylpropylol ether, divinyl ether, vinylbutylol ether and vinylbenzylalcohol ethers.

Preferably, compound (B) in the composition according to the invention is halogen-free.

In addition, the composition preferably contains one or more antioxidants, such as hydroxybenzophenone, esters of salicylic acid and hydroxyphenylbenzotriazoles.

The composition preferably contains mould release agents. In addition, the composition preferably contains one or more inhibitors in amounts between 0,005 and 0,2 wt.-%, in particular between 0,01 and 0,1 wt.-% with respect to the total composition weight. Known inhibitors that may be used are for example of the quinone type.

The initiator system is preferably chosen from the group consisting of peroxides, perketals and percarbonates. Examples are hydrogen peroxide, benzoyl peroxide, t-butyl peroxide, t-butyl peroctoate, t-butyl perbenzoate, dicumyl peroxide, di-t-butyl peroxide, trimethylcyclohexanone perketal, methylethylketone peroxide, acetylacetone peroxide, cyclohexanone peroxide, methylisobutylketone peroxide, and diacetonealcohol peroxide.

Furthermore, catalysts may be added, for instance octoates or naphthenates of copper, lead, calcium, magnesium, cerium, and in particular of manganese and cobalt, or vanadium complexes. Promotors may also be added to these accelerators, for instance acetylacetone. Aromatic amines such as dimethylaniline, diethylaniline and/or dimethylparatoluidine may also be

used as catalysts.

The preferred unsaturated polyester resin (A) is halogen-free. Particularly preferred resin compositions are those in which the said unsaturated polyester resin (A) is an unsaturated polyester resin, substantially free of aromatic acid moeities in the backbone. These resins are for instance based on an alkylene glycol, such as propylene glycol, and a non-aromatic carboxylic acid or its anhydride, such as maleic acid (anhydride).

Another family of preferable unsaturated resin compositions are those comprising as component (A) an unsaturated polyurethane polyacrylate or polymethacrylate resin and at least one other ethylenically unsaturated polyester copolymerisable therewith, and wherein said component (B) comprises an alkyl methacrylate monomer. These resin compositions, which will from now on be referred to as urethane (meth)acrylate resins, are for instance described in US Patent 4,480,079 (1984) and in US Patent 5,126,396 (1992), hereby incorporated by reference. Compositions according to the invention and based on these urethane (meth)acrylate resins particularly yield a high flammability resistance.

In addition it is advantageous to characterize the resin composition by being substantially free of a char-forming additive. Char-forming additives are well known in the art of flame-retardancy. These carbon-sources are generally materials having many radicals capable of entering into an esterification reaction with phosphoric acid. They generally have a high carbon content and decompose at higher temperatures than the phosphoric acid source. Typical examples of char-formers are starch, casein, glucose, and polyvalent alcohols, such as pentaerythritol, dipentaerythritol, tripentaerythritol, and mixtures thereof. The char-former free embodiment

has excellent environmental resistance, and surprisingly a high flammability resistance.

The melamine to be used as component (C) in the composition of the invention is a definite compound, 2,4,6-triamino-1,3,5-triazine, a common article of commerce. It is preferably used in finely divided, in particular powdered, form. It is within the broader scope of the invention to use crude melamine and/or polycondensed melamines, such as melam, melem and melon. These are melamines with two or three triazine rings, obtainable by condensation of melamine in the presence of a suitable catalyst, such as $ZnCl_2$. It is also possible to use compounds like ammeline, ammelide and their condensation products.

The phosphorus compound (D) in the composition according to the invention is any ester of phosphorus acids, or any salt of phosphorus acids with nitrogen-based cations, or phosphoric acid itself, such as orthophosphoric acid, pyrophosphoric acid or polyphosphoric acid.

A preferred group of phosphorus compounds, because of the convenient viscosity-lowering effect, are tetracoordinate phosphorus esters having viscosities lower than that of the unsaturated resin itself. By tetracoordinate compound is meant a compound with four atoms attached to the phosphorus atom. Examples of such volatile phosphorus esters are triethyl phosphate, dimethyl methylphosphonate, diethyl ethylphosphonate and homologs thereof.

Another family of phosphorus compounds which, together with melamine, are effective flame retardants, in the compositions of the invention, are ammonium phosphate, ammonium pyrophosphate, ammonium polyphosphate, ethylenediamine phosphate, piperazine phosphate, piperazine pyrophosphate, melamine phosphate, dimelamine phosphate, melamine pyrophosphate, melamine metaphosphate, guanidine

phosphate, dicyandiamide phosphate, and/or urea phosphate.

It is also possible to use as phosphorus compound (D), a phosphoric acid, that is, one or more acid tetracoordinate phosphorus compounds such as orthophosphoric acid, pyrophosphoric acid, polyphosphoric acid or a partial ester thereof such as methyl acid phosphate, ethyl acid phosphate, butyl acid phosphate, amyl acid phosphate, dibutyl acid pyrophosphate and the like, which in the presence of the melamine, will become converted to a melamine salt. To have the requisite amount of melamine, required by the invention, melamine should be added in amounts equal to or in excess of the amount which will form a salt with the phosphoric acid, i.e. in amounts equal to or in excess of the amount equivalent to the phosphoric acid on a molar basis. A preferred phosphoric acid is the compound known in the fertilizer art as superphosphoric acid, this being a substantially anhydrous liquid phosphoric acid with a small pyrophosphoric acid content. This acid is readily available in commerce, for example from Texas Gulf Corp.

A particularly preferred resin composition comprises a combination of effective amounts of melamine, a volatile phosphorus ester, preferably triethyl phosphate or dimethyl methylphosphonate, and superphosphoric acid. In this embodiment preferably equimolar amounts of melamine and superphosphoric acid are used, since this yields excellent flame retardancy and low corrosivity. Moreover flame retardant synergism is observed between the triethyl phosphate and the superphosphoric acid in such compositions. The preferred relative amounts for this embodiment are from 15-25 wt.-% melamine, from 5-15 wt.-% superphosphoric acid and from 0,1-5 wt.-% volatile phosphorus ester.

A particularly preferred resin composition

according to the invention comprises as component (D) a combination of a low viscosity liquid phosphorus compound chosen from the group consisting of triethyl phosphate, dimethyl methylphosphonate and homologs thereof, and a phosphorus compound chosen from the group consisting of phosphoric acid and superphosphoric acid. This resin composition exhibits a synergistic interaction between the two phosphorus compounds leading to superior flame retardancy. This is particularly the case for resin compositions wherein the unsaturated polyester resin (A) is an unsaturated polyester resin, substantially free of aromatic acid moeities in the backbone, or for resin compositions, wherein said unsaturated polyester resin (A) is a urethane (meth)acrylate resin.

The effective quantity of melamine is in the range of 15-70 wt.-% of the total unsaturated resin composition weight. The preferred quantity is 20- 60 wt.-%. The effective quantity of the phosphorus compound is in the range of 0,25-25 wt.-% of the total unsaturated resin composition. The preferred quantity is 0,5-20 wt.-%. Most preferred is 2-10 wt.-%. The total amount of the melamine and the phosphorus compound should preferably not exceed about 70 wt.-%, otherwise the mechanical properties of the composition may be affected in a negative sense.

While it is a feature of the invention that halogens and alumina trihydrate are not needed, they can be present in the broader scope of the invention. Thus, the unsaturated resin can be one based on, for instance, tetrabromophthalic acid and/or tetrachlorophthalic acid, and/or chlorendic acid, and/or diol esters of these acids, and/or dibromoneopentyl glycol and/or the bis(hydroxyethyl) ether of tetrabromobisphenol-A.

Alumina trihydrate can be used as a supplemental flame retardant or for aesthetic reasons

such as to obtain an artificial marble or onyx effect. Other mineral fillers can be used for like reasons, for example gypsum (calcium sulfate), mica, talc, clays, and calcium carbonate. A particularly advantageous feature of the compositions of the invention is the use of melamine and the phosphorus compounds mentioned above, in combination with calcium carbonate and/or calcium sulfate (gypsum), which compositions are preferred. Such compositions afford a particularly high level of flame retardancy. This is surprising since it is well known to the skilled person in the art of flame retardancy that for instance calcium carbonate interferes with other flame retardants. When a combination of melamine, a phosphorus compound and calcium carbonate and/or calcium sulfate is used, the preferred phosphorus compound is a neutral ester, such as for example triethyl phosphate. Preferably the resin composition comprises between 10-30 wt.-% of melamine, between 30-50 wt.-% of calcium carbonate and/or calcium sulfate, and between 2-10 wt.-% of phosphorus compound, all wt.-% being with respect to the total weight of the resin composition.

Another particularly advantageous feature of the compositions of the invention is that it is even possible to use melamine, in combination with calcium carbonate and/or calcium sulfate (gypsum), without subtantial amounts of the phosphorus compounds mentioned above. Such compositions surprisingly yield a high level of flame retardancy, and synergism between melamine and the calcium carbonate and/or calcium sulfate is observed. Preferably such a resin composition comprises between 20-40 wt.-% of melamine, and between 20-40 wt.-% of calcium carbonate and/or calcium sulfate, with respect to the total weight of the resin composition.

Blending the ingredients of the composition according to the invention can be conducted by any

means suitable for the uniform dispersion of a generally viscous resin with particulate solids, such as mixing in with a rotary stirrer or a Banbury mixer.

The resin mixtures of the invention may also have other ingredients such as pigments, stabilizers, processing aids, coupling agents, lubricants, mold release agents, and electroconductive additives. Likewise they may contain reinforcing additives such as glass fibers, mineral fibers, carbon fibers, aramide fibers, wollastonite, and the like. Minor amounts of thermoplastics may also be admixed with the resin, such as low profile additives to create a smooth surface of the moulded product and reduce or prevent shrinkage upon cure.

The invention also relates to a flame retarded intermediate comprising a resin mixture of (A) an unsaturated polyester resin, (B) a vinyl monomer copolymerizable with said resin (A), the usual additives and reinforcing fibres, the resin mixture being thickened, characterized in that, it further comprises an effective flame retardant amount of (C) melamine and (D) a phosphorus compound. The thickening reaction is usually effected by adding metal oxides and metal hydroxides such as MgO and $Mg(OH)_2$, in an amount of 1-10 wt.-%, based on the resin mixture. A maturation period, during which the unsaturated polyester resin is thickened, is usually observed before the intermediate is moldable into end-products. Glass fibre, in the form of continuous fibres or as fibres with lengths between 0,5 mm and 5 cm, is usually used as reinforcing fibre in an amount between 30 and 300 parts by weight based on the resin mixture. Additionally, polyester, carbon, aramid, and acrylic fibres, for example, may also be used. The usual additives, which are used in 50-500 parts by weight, based on the total of components (A) and (B), are, for instance, chalk, talc, silica and carbon black. These fiber reinforced unsaturated resin

compositions are usually referred to in the open literature as Sheet Molding Compound (SMC), Bulk molding Compound (BMC), Thick Molding Compound (TMC) and other similar denotations.

The resin compositions according to the invention can easily be molded into end products by all known processing methods. Suitable processing methods are for instance injection molding, compression molding or a combination of the two, as well as methods such as hand layup, spray-up, filament winding and pultrusion. End products typically manufactured with the composition according to the invention are components for the transport industry, such as for instance truck or car hoods, boat hulls and bulkheads, aircraft cabin bulkheads, components for the electronical and electrical industry, such as for instance connector housings, and components for the building industry, for example large panels or profiles.

EXAMPLES

To further clarify the compositions and methods of the invention, and to illustrate the best mode of carrying it out, the following examples are given.

The materials used are as follows :

Modar™ - 814 : an unsaturated urethane methacrylate resin, containing 38-42 wt.-% of polyurethane polyacrylate polymer, 13 wt.-% of styrene, and 47 wt.-% of methyl methacrylate. Specific gravity 1,040 - 1,060 at 255°C. Obtainable from Ashland Chemical, Inc.

Vibrin™ V51-708 : an aliphatic unsaturated polyester resin from propylene glycol and maleic acid, obtained from Corning Fiberglass Canada, Inc.

Synolite™ 0020-N-1, an unsaturated polyester

resin from DSM Resins, The Netherlands.

ATH : SB - 336, a medium particle size aluminum trihydrate having 64,9 wt.-% Al_2O_3, particle size 33 wt.-% less than 10 microns, bulk density : 0,75 g/cm³ loose, surface area : 1,5 m²/g, oil absorption 23 ml/100 g of filler, 87 % TAPPI brightness from J.M.Huber Corporation.

Micral™ - 932 : a high surface area aluminum trihydrate having 64,9 wt.-% Al_2O_3, particle size 100% through 325 mesh, bulk density : 0,5 g/cm³ loose, surface area : 13 m²/g, oil absorption 38 ml/100 g of filler, 95 % TAPPI brightness from J.M.Huber Corporation.

Melamine - 003 : a fine particle grade melamine from DSM Melamine Americas, Inc.

Triethyl Phosphate : a colorless liquid from Eastman Chemical Company.

Fyrol™ DMMP : dimethyl methylphosphonate, a colorless liquid from Akzo Chemicals.

Ammonium polyphosphate : Amgard™ MC, a white powder from Albright & Wilson.

Melamine orthophosphate : a white powder, obtained from DSM Chemicals, the Netherlands.

Melamine - ultrafine : a melamine from DSM Melamine Americas, Inc.Dimelamine Phosphate : from DSM Melamine Americas, Inc..

SPA : Superphosphoric Acid, Super™-49 from Texas Gulf Corp., 72% P_2O_5 content, greenish liquid.

Vicron™ 15-15 : a ground calcium carbonate (average particle diameter 3 μm) from Pfizer Minerals Inc.

<u>Examples 1-30</u>

Of these Examples 1-30, Examples 11, 12, 14-18, 20, 22, 24, 26, 27 and 29 are according to the invention. Examples 1-10, 13, 19, 21, 23, 25, 28 and 30 are Comparative Experiments (marked with an "*" in

Tables 1-2).

All components were mixed in the relative quantities as indicated in Tables 1-2 using standard mixing equipment. Test bars were made from the compositions by pouring the prepared compositions in a mould and curing in an oven at the cure temperature, given by the manufacturer of the resin. Some bars were post cured during 24 hrs at the recommended post cure temperature.

Flammability was tested by subjecting the test bars to the UL-94 test (Underwriters Laboratories). The Oxygen Index (OI) values were determined according to ASTM D 2863-77. The UL-94 test involved preparation of 5 standard test bars with a thickness of 3,2 mm, which were ignited by a standard flame from the bottom and their post-flame-exposure "after-flame" burning times noted. The target rating is "VO" which means that the average after-flame time is 5 sec. or less, and no one bar burns over 10 sec.. Also no flaming drip is permitted.

The obtained flammability results are summarized in Tables 1-6.

The salient points of the obtained results with the MODAR™ resin based compositions are as follows.

Comparative Experiment 10 shows that 10 wt.-% triethyl phosphate by itself without melamine gives a complete burn in the UL-94 test. It also interferes with the cure; the resin with triethyl phosphate at 10 wt.-% is very soft (Comp. Ex. 10, Barcol hardness 2-6, compared with 38-42 without triethyl phosphate (Comp. Ex. 1)). Even as little as 2 wt.-% triethyl phosphate (Comp. Ex. 8) retards the room temperature cure perceptibly (Barcol hardness 20-22 vs. 22-25 without). On the other hand, a combination of 30 wt.-% melamine and 2 wt.-% triethyl phosphate gave a VO rating (Ex. 20). Curing time was 24 hours at room temperature for

Ex. 20 whereas by contrast, 30 wt.-% ATH and 2 wt.-% triethyl phosphate required over 72 hours (Comp. Ex. 21). A VO result was also obtained with 1 wt.-% triethyl phosphate with 25 wt.-% melamine and 15 wt.-% ATH (Ex. 18).

The salient points of the results with the VIBRIN™ based resin compositions are in the comparison of triethyl phosphate with melamine (the present invention) to triethyl phosphate with ATH (prior art) as follows : 3 wt.-% triethyl phosphate with 30 wt.-% melamine gave a room temperature cure in 24 hours and a VO result (Ex. 24), whereas 3 wt.-% triethyl phosphate with 30 wt.-% ATH gave a cure time of over 72 hours and failed the UL-94 test (Comp. Ex. 25). With 30 wt.-% melamine, using, in place of the triethyl phosphate, 2 wt.-% dimethyl methylphosphonate gave a VO rating (Ex. 26, borderline since one bar exceeded 10 sec.). Using 30 wt.-% melamine and 2 wt.-% ammonium polyphosphate gave VO and a 24 hr. curing time (Ex. 27). Using 2 wt.-% melamine phosphate and 30 wt.-% melamine gave a firm VO and cured in 24 hours (Ex. 29). By contrast, 30 wt.-% ATH with either 2 wt.-% melamine phosphate or 2 wt.-% ammonium polyphosphate failed the UL-94 test (Comp. Ex. 30).

A specific gravity advantage was observed with the 2 wt.-% melamine phosphate plus 30 wt.-% melamine formulation; its specific gravity was 1,2875 (Ex. 29) whereas with 2 wt.-% melamine phosphate plus 30 wt.-% ATH, the specific gravity was 1,5413 (Comp. Ex. 30). Also, the formulation with the melamine was more viscous (kinematic viscosity of 98,5 Stokes at room temperature whereas with ATH it was 55,4 Stokes); the ATH formulation settled much faster and required more stirring.

A further major advantage noted with the triethyl phosphate plus melamine formulations over the triethyl phosphate plus ATH formulations is that the

melamine formulations visibly give less smoke, and form a much sturdier char barrier indicating that they can bear greater heat loads than the ATH formulations.

These examples are presented for purposes of illustration and are not intended to be limiting. Within the scope of the invention are further formulations having additionally such additives as stabilizers, colorants, processing aids, low profile additives, delustrants, fillers such as calcium carbonate and gypsum, and other flame retardants such as halogenated additives, borates, molybdates, magnesium hydroxides, stannates, other melamine salts (borate, oxalate, sulfate, pyrophosphate, and the like) which may supplement or synergise with the flame retardant additives of the invention.

Table 1: Flammability data of cured Modar^{TM} - 814 unsaturated resin with additives

Exp.No.	Additives	wt.%	LOI	Average Barcol Hardness [1]	Average burning times (UL-94)[2]
1*	None	00	17.6	24 / 40	Burn to clamp
2*	ATH	30	23.4	35 / 57	Burn to clamp
3*	ATH	70	43.3	63 / 69	0.00 /0. 00
4*	Melamine 003	30	25.2	24 / 41	Burn to clamp
5*	Melamine 003	70	32.9	43 / 51	0.00 / 0.00
6*	Melamine 003	20	22.7	23 / 40	Burn to clamp
7*	ATH	20	22.4	30 / 55	Burn to clamp
8*	Triethyl Phosphate	02	27.1	21 / 36	Burn to clamp
9*	Triethyl Phosphate	05	30.0	19 / 30	Burn to clamp
10*	Triethyl Phosphate	10	27.6	03 / 04	Burn to clamp
11	Triethyl Phosphate Melamine 003	02 40	28.1	31 / 40	0.00 / 1.60
12	Triethyl Phosphate Melamine 003	05 30	29.0	23 / 35	0.00 / burn to clamp
13*	Triethyl Phosphate ATH	05 30	29.8	24 / 43	Burn to clamp
14	Triethyl Phosphate Melamine 003 ATH	08 15 15	27.8	12 / 20	0.00 / 0.00
15	Triethyl Phosphate Melamine 003 ATH	05 20 20	29.1	18 / 30	0.00 / 0.00
16	Triethyl Phosphate Melamine 003 ATH	02 15 25	28.3	29 / 34	0.00 / 3.20
17	Triethyl Phosphate Melamine 003 ATH	02 25 15	28.0	13 / 27	0.00 / 0.00

Exp.No.	Additives	wt.%	LOI	Average Barcol Hardness [1]	Average burning times (UL-94)[2]
18	Triethyl Phosphate Melamine 003 ATH	01 25 15	27.6	22 / 33	0.00 / 6.00
19*	Melamine 003 ATH	15 15	26.7	22 / 33	3.20 / burn to clamp
20	Triethyl Phosphate Melamine 003	02 30	28.6	18 / 33	0.00 / 5.60
21*	Triethyl Phosphate ATH	02 30	27.2	21 / 37	0.00 / 21.4
22	Triethyl Phosphate Melamine 003	03 30	28.8	16 / 30	0.00 / 3.00

[1] : Average of 10 specimen (cured/postcured for 24 hrs)
[2] : Average of 5 specimen on first ignition/second ignition

Table 2: Flammability data of cured Vibrin™ V51-708 unsaturated resin with additives

Exp.No.	Additives	wt.%	LOI	Average Barcol Hardness [1]	Average burning times (UL-94)[2]
23*	None	00	18.3	25 / 42	Burn to clamp
24	Triethyl Phosphate Melamine 003	03 30	27.6	18 / 29	0.00 / 0.00
25*	Triethyl Phosphate ATH	03 30	24.2	21 / 37	0.00 / burn to clamp
26	Fyrol DMMP Melamine 003	02 30	26.2	19 / 31	0.20 / 8.40
27	Amgard MC Melamine 003	02 30	27.6	27 / 37	0.00 / 1.80
28*	Amgard MC ATH	02 30	25.3	31 / 41	1.40 / burn to clamp
29	Melamine-orthophosphate Melamine 003	02 30	26.2	26 / 37	0.00 / 0.80
30*	Melamine-orthophosphate ATH	02 30	22.7	30 / 40	4.40 / burn to clamp
31	Melamine 003 Superphosphoric acid	30 1.68	26.4	14 / 32	0.00 / 0.00
32	Melamine 003 Superphosphoric acid	21.6 8.4	26.5	12 / 30	0.00 / 1.60
33	Melamine 003 Superphosphoric acid Cobalt Naphtenate Cadox L-50	20 3.2 0.1152 1.536	27.6	- / 47	0.00 / 0.00
34	Melamine 003 Superphosphoric acid Cobalt Hex-cem Cadox L-50	20 3.2 0.3072 1.536	26.2	- / 39	0.00 / 2.60

[1] : Average of 10 specimen (cured/postcured for 24 hrs)
[2] : Average of 5 specimen on first ignition/second ignition

Examples 31-34

All resins were tested according to the same procedure as in Examples 1-30.
The obtained flammability results are summarized in Table 2.

Examples 35-37

Of these Examples 35-37, Examples 36 and 37 are according to the invention. Example 35 is a Comparative Experiment (marked with an "*" in Table 3).

All resins were tested according to the same procedure as in Examples 1-30.
The obtained flammability results are summarized in Table 3.

Table 3:
Flammability data of cured Synolite™ 0020-N-1 unsaturated resin with additives

Exp.No.	Additives	wt.%	LOI	Average Barcol Hardness [1]	Average burning times (UL-94)[2]
35*	Melamine 003 Vicron 15-15 Cobalt Hex-cem Cadox L-50	20 40 0.032 0.8	24.9	27 / 60	0.00 / burn to clamp
36	Melamine 003 Triethyl Phosphate Vicron 15-15 Cobalt Hex-cem Cadox L-50	20 05 40 0.028 0.7	28.7	- / 38	0.00 / 0.00
37	Melamine 003 Superphosphoric acid Cobalt Hex-cem Cadox L-50	20 3.2 0.307 2 1.536	24.4	- / 42	8.40 / burn to clamp

[1] : Average of 10 specimen (cured/postcured for 24 hrs)
[2] : Average of 5 specimen on first ignition/second ignition

Examples 38-41

Of these Examples, Examples 39-41 are according to the invention. Example 38 is a Comparative Experiment (marked with an "*" in Table 9).

A series of four resin compositions (BMC compounds) was prepared on a Z-blade mixer from the company Werner & Pfleiderer and molded into flat plaques for investigation of flame retardant behaviour and density. The compositions consisted of the following basic components (in parts by weight) :

75	pbw	Synolite™ 0020-N-1, an unsaturated polyester resin from DSM Resins, The Netherlands.
25	pbw	Synolite™ 7223-M-1, an unsaturated polyester resin from DSM Resins, The Netherlands.
5	pbw	Coathylene™ HA 1681 from Plastlabor, Germany.
5	pbw	Zinc Stearate as mold release agent.
1	pbw	Trigonox™ C, a peroxide catalyst from Akzo, The Netherlands.
3,5	pbw	Luvatol MK25, a resin thickener (Magnesium Oxide)
8,7	pbw	white pigment paste

and in addition variable amounts of

TEP	Triethyl Phosphate, from Fluka Chemie.
ATH-1	Martinal™ OL104, an Alumina Trihydrate from Martinswerke, Germany.
ATH-2	Martinal™ ON310, an Alumina Trihydrate from Martinswerke, Germany.
ATH-3	Martinal™ ON906, an Alumina Trihydrate from Martinswerke, Germany.
Mel	Melamine 003, from DSM Chemicals, The Netherlands.
Reinf	Glass fiber chopped strand (6 mm average length) from Owens Corning.

in the following quantities (pbw) given in Table 4:

Table 4: Relative amounts of flame retardant ingredients in Experiments 38-41

Exp.No.	TEP	ATH-1	ATH-2	ATH-3	Mel	Reinf
38*	-	38	75	-	-	79.2
39	12.5	-	-	-	125	87.4
40	8	-	-	-	80	70.9
41	5	-	-	75	50	84.9

Compound 38 contains 50 wt.-% ATH, based on the resin composition weight without the glass fiber reinforcement (the paste weight). Compounds 38, 39 and 40 contain a decreasing amount of melamine (50, 40 and 30 wt.-% on paste weight) as filler, all in combination with TEP (10 wt.-% with respect to the melamine weight). Finally, compound 41 comprises a combination of melamine/TEP and ATH as filler. All compounds contain 25 wt.-% of chopped glass strands.

After a maturation period of one week, in which period the compounds were sufficiently thickened, the compounds were compression molded (150°C, 100 bar) into flat plaques (25x25cm) of 3,2 mm thickness. From these plaques the densities were determined according to ASTM D 792-91 and samples were cut for flame retardancy tests.

The measured flame retardant properties were the Limiting Oxygen Index (LOI, ASTM D 2863-77) and the UL94 test (vertical testing at 3,2 mm thickness).

The results obtained are summarized in Table 5.

Table 5: Flammability results

Exp.No.	Density (g/cm^3)	LOI (-)	UL-94 classification
38*	1.67	27.5	NC (3x V-0)
39	1.47	27.5	V-0
40	1.43	25	NC (3x V-0)
41	1.60	27.5	V-0

* : Comparative Experiment
NC: No classification

The combination of melamine and TEP in the compound according to the invention yields a better UL94 performance (Ex. 40 and 41) than the corresponding BMC compound with ATH as flame retarding agent (Comp. Ex. 38).

WHAT IS CLAIMED IS

1. A flame retarded thermosetting resin composition comprising (A) an unsaturated polyester resin and (B) a vinyl monomer copolymerizable with said resin (A), characterized in that, it further comprises an effective flame retardant amount of (C) melamine and (D) a phosphorus compound, and is substantially free of halogen and an unesterified polyol.
2. A resin composition according to claim 1, characterized in that it is substantially free of a char-forming additive.
3. A resin composition according to claim 1 or 2, characterized in that, the phosphorus compound (D) is a low viscosity liquid phosphorus compound chosen from the group consisting of triethyl phosphate, dimethyl methylphosphonate and homologs thereof.
4. A resin composition according to any one of claims 1-3, wherein said phosphorus compound (D) is chosen from the group consisting of ammonium phosphate, ammonium pyrophosphate, ammonium polyphosphate, ethylenediamine phosphate, piperazine phosphate, piperazine pyrophosphate, melamine phosphate, dimelamine phosphate, melamine pyrophosphate, melamine metaphosphate, guanidine phosphate, dicyandiamide phosphate, and/or urea phosphate, phosphoric acid and superphosphoric acid.
5. A resin composition according to any one of claims 1-4, further comprising calcium carbonate and/or calcium sulfate.
6. A resin composition according to any one of claims 1-5, characterized in that it comprises an effective flame retardant amount of melamine, a volatile phosphorus ester, and superphosphoric

acid.

7. A resin composition according to claim 1, wherein said melamine (C) is present in an amount of 20-60 wt.-% and said phosphorus compound (D) is present in an amount of 0,5-20 wt.-%, the weight percentages being relative to the sum of components (A) to (D).

8. A resin composition according to any one of claims 1-7, further comprising alumina trihydrate.

9. A semi-finished product, comprising reinforcing fibres and a resin composition according to any one of claims 1-8.

10. Shaped articles, made from a resin composition according to any one of claims 1-9.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PC1/NL 97/00076

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/3492 C08L67/06 C08K5/49 C08K3/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 308 699 A (HOECHST) 29 March 1989 see claims 1,10,20; examples 1,2,64; tables ---	1,4,7-9
A	US 5 312 846 A (SMITS ET AL.) 17 May 1994 see column 3, line 16 see column 8, line 22 - line 23; example 1 ---	1,3
A	DE 44 26 010 A (CHEMIE LINZ) 9 February 1995 see claims 1,10; example 4 ---	1,3,7
A	US 4 257 931 A (GRANZOW) 24 March 1981 see column 1, line 58 - column 2, line 62; claims 1-3 --- -/--	1,3-5

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

2

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	FR 2 225 501 A (UNIVERSAL-RUNDLE) 8 November 1974 see claims 1,5-8; examples ---	1,2,8,9
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2

INTERNATIONAL SEARCH REPORT

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